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(71) Applicant (*for all designated States except US*): MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): PATEL, Ranjan, C. [GB/GB]; George Green Cottages, Little Hallingbury, Essex CM22 7PP (GB). SOUTER, John [GB/US]; 185 Bederwood Drive, Orono, MN 55356 (US). ZWADLO, Gregory, L. [US/US]; 367 N. Maple, Ellsworth, WI 54011 (US). CHAMBERS, Mark, R., 1. [GB/GB]; 10 Cranberry Lane, London E16 4PE (GB). VOGEL, Jonathan, C. [GB/GB]; 29 Barley Croft, Harlow, Essex CM18 7RU (GB).

(74) Agents: GWIN, H., Sanders et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

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(54) Title: HALF-TONE IMAGING BY LASER-INDUCED FILM TRANSFER TO TEXTURED RECEPTOR

(57) Abstract

A method of imaging is provided. The method of half tone imaging comprising the steps of: (a) assembling in mutual contact a receptor sheet and a colorant donor sheet, said colorant donor sheet comprising a support bearing a thermofusible colorant layer comprising a binder, a colorant and an absorber; (b) exposing the assembly to scanned laser radiation of a wavelength absorbed by said absorber, said laser radiation being focussed to a spot of area A μm^2 at the plane of the colorant transfer layer and being modulated in accordance with digital half tone image information, and thereby causing exposed portions of the colorant layer to soften or melt and adhere preferentially to the receptor sheet; (c) peeling apart said receptor sheet and colorant donor sheet; characterize in that said receptor sheet comprises a support having a textured receptor layer surface comprising a plurality of protrusions projecting above the plane of the outer surface of said receptor layer by an average distance of no greater than about 8 μm, there being on average at least 1 of such protrusions per area of A μm^2.

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HALF-TONE IMAGING BY LASER-INDUCED FILM TRANSFER TO TEXTURED RECEPTOR

Field of the Invention

This invention relates to a method of imaging in which a thermofusible colorant is transferred from a donor to a receptor under the influence of laser radiation. In particular, the invention relates to such an imaging method in which the receptor comprises a surface texture that is optimized for the "footprint" of the exposing laser.

Background of the Invention

There is continuing interest in imaging by means of laser-induced colorant transfer from a donor element to a receptor. The donor elements typically comprise a support bearing, in one or more coated layers, an absorber for the laser radiation, a transferable colorant (e.g., one or more dyes or pigments) and one or more binder materials. When the donor element is placed in contact with a suitable receptor and subjected to a pattern of laser irradiation, absorption of the laser radiation causes rapid build-up of heat within the donor element, sufficient to cause transfer of colorant to the receptor in irradiated areas. By repeating the transfer process using different donor elements but the same receptor, it is possible to superimpose several monochrome images (e.g. yellow, magenta, cyan and black color separations) on a common receptor, thereby generating a full-color image. The process is ideally suited to the output of digitally stored image information, and has the additional benefits of not requiring chemical processing, and not employing materials that are sensitive to normal white light.

There are two main classes of laser stimulated colorant transfer from a donor to a receptor, namely dye sublimation transfer and mass transfer. In the former, image dyes diffuse or sublime in response to laser-generated heat, but the physical integrity of the donor layer is not affected. In the latter, portions

of the donor layer (i.e., binder and colorants and absorber, if present) transfer *en masse* to the receptor. Different types of image are available by these different mechanisms. Dye sublimation may give a continuous tone image in which the density of the transferred image varies over a significant range with the energy absorbed. Mass transfer typically gives a bi-level image in which either zero or maximum density is transferred, depending on whether the applied energy exceeds a given threshold. Mass transfer systems are therefore ideally suited to the reproduction of half tone images.

This basic distinction between the two classes was recognized since at least the mid 1970's and is disclosed in JP-51-88016. This reference deals primarily with sublimation transfer, and distinguishes the situation in which dye alone is transferred from the situation in which both dye and binder are transferred. The same distinction has been applied consistently in the art, up to and including recently-issued patents, such as, US-A-5,516,622.

Records of laser-induced mass transfer date from at least the 1960_s. For example, JP-46-3710, which was filed in 1966, discloses transfer of colorant from a donor to a receptor by a "sputtering" process mediated by laser exposure. Coatings of printing ink on plastic film are quoted as highly suitable donor sheets.

A paper published in 1970 (Applied Optics, 9 (No. 10), pp. 2260- 2265) distinguishes two modes of laser mass transfer, namely a less energetic mode in which transfer occurs in a fluid state (i.e., melt transfer), and a more energetic mode in which transfer occurs by an explosive force, as a result of generation and rapid expansion of gases at the substrate-coating interface (i.e., ablation transfer). This distinction is also recognized consistently by later authors. For example, US-A-5,156,938, US-A-5,171,650, US-A-5,516,622 and US-A-5,518,861 all refer to ablation transfer as a process distinct from melt transfer, and emphasize its explosive nature. The first two patents in particular emphasize the use of thermally degradable materials to assist with the transfer process. Many other patents, such as US-A-3,962,513, refer to the use of nitrocellulose or "self-oxidizing" binders in ablation transfer.

Conversely, other patents, such as JP-69-319192, EP-A-530018, US-A-5,501,937, US-A-5,580,693, US-A-5,401,606 and US-A-5,019,549, refer to transfer of colorant in a molten or semi-molten (softened) state, with no mention of explosive mechanisms. Many of the known laser-induced melt transfer materials employ one or more waxes as binder materials, in pursuit of a transfer layer which melts sharply to a highly fluid state at moderately elevated temperatures.

However, it has been shown recently that excellent image quality is provided by a melt transfer system in which the colorant layer transfers essentially in the form of a coherent film, and does not apparently achieve a state of high fluidity during the transfer process. Indeed, this transfer mechanism - laser-induced film transfer (LIFT) - is promoted by the inclusion in the transfer layer of compounds which effect at least a partial curing (and ultimately hardening) of that layer during the transfer process, as described in British Patent Application No. 9617414.9 entitled "Crosslinkable Media Imageable by Laser Irradiation," filed August 20, 1996.

Transfer of the colorant layer in the form of a coherent film enables dots or pixels to be transferred to the receptor with excellent edge definition. Furthermore, the curing that occurs in the course of the transfer leads to an image of enhanced durability with excellent overprint characteristics, i.e., it is possible to transfer second and subsequent images to a common receptor without damaging the first image transferred thereto. Both of these factors are important in the successful development of a digital half-tone imaging system based on laser-induced colorant transfer.

Under carefully controlled laboratory conditions, small-area images of excellent quality are formed by the LIFT process using conventional smooth receptors such as resin-coated paper. However, when the imaging is carried out in a less well-controlled environment, the image quality is found to deteriorate markedly, with voids appearing (apparently) at random in the transferred image. The problem may be traced to the presence of dust particles on the surfaces of the donor and receptor. Such particles not only prevent effective

contact of the donor with the receptor in their immediate vicinity, but also adversely affect the focusing of the laser by causing bumps or undulations in the absorbing layer, so that even small dust particles can give rise to significant "dropouts." The problem is particularly acute in the case of large area images (e.g., of A2 size), where the likelihood of attracting dust on to the surfaces of the sheets is greater due to the triboelectric charging that inevitably results from the handling of such large sheets. The lamination of smooth sheets in consistent mutual contact, without forming pockets of trapped air, also becomes increasingly difficult as the area of the sheets increases.

US-A-5,580,693 describes the problems caused by poor contact between donor and receptor (e.g., due to dust particles) in a melt transfer process, and proposes as a solution the provision, in the donor element, an additional deformable or "cushioning" layer. The addition of such a layer adds significantly to the manufacturing costs.

Since the presence of dust cannot be eliminated under normal working conditions, there is a need for alternative means of ensuring effective contact between a colorant donor and a receptor that is compatible with transfer of the colorant as a coherent film and also tolerant of the presence of dust particles.

There is a long history of using beads or other inert particles in photographic materials for various purposes, such as for matting purposes, or for spacing purposes, e.g., to prevent adjacent sheets in a stack from sticking together. They have also found widespread use in materials intended for contact exposure, e.g., to promote good vacuum draw-down or to suppress interference fringes resulting from close contact of films. These uses are documented in US-A-4,711,838 and elsewhere.

The use of particulate matter in adhesive layers for anti-blocking characteristics is known. A specific example of using organic polymeric beads with a narrow molecular weight distribution in an adhesive layer of a surprint color proof is described in US-A-4,885,225. In this particular application, the size of the polymeric beads is kept small enough to become encapsulated into the adhesive when the proofing film is laminated to an opaque substrate; and

thus, the beads have little or no effect on the visual properties of the final imaged proof.

The use of organic polymeric beads with a narrow molecular weight distribution in a protective layer of an overlap color proof is described in US-A-5,258,261. The protective layer in this application is removed during the imaging process; and therefore, the beads would have no visual effect on the final image of the proof.

The use of organic polymeric beads have also been shown to reduce the effects of Newton's rings when a film is contacted with reproduction media during the exposure process. A specific example of this application is described in US-A-2,992,101.

Organic polymerio beads dispersed in a water-based receptive coating have also been shown to be useful in electrostatic transparencies imaged in plain paper copiers. Specific examples of this application are described in US-A-5,310,595 and US-A-4,869,955. In these applications the image is transferred onto the receptive layer containing the polymeric beads.

In the field of dye sublimation transfer, it has been known since at least the mid 1970's that spacing apart of the donor and receptor is necessary (see, for example, JP-51-88016). Also, US-A-4,541,830 and US-A- 4,777,159 disclose the use of beads or other non-sublimable particles for this purpose. The beads are dispersed within the dye layer, but are of sufficient size to project outwardly from it. US-A-4,772,582 and US-A-4,876,235 disclose the use of beads coated on top of the dye layer,and the use of beads in the receptor layer, respectively. US-A-5,017,547 discloses the use of vacuum hold-down of donor to receptor, one of which contains spacer beads. The provision of a "textured surface" between donor and receptor, the texture being generated by embossing or other suitable means not involving the use of added particulates, is disclosed in US-A-5,254,514. It is noteworthy that many of these patents describe the primary purpose of the beads or other spacing means as being to *prevent* adhesion of donor layer to receptor layer. The APPROVAL digital color proofing system, commercially available from Kodak, is based on dye

sublimation transfer, and utilizes a receptor sheet comprising beads in the receptor layer. Microscopic analysis indicates that the beads are about 20 μm in diameter and are present at a coverage of no more than about 100 beads per mm^2.

Spacer beads have also been advocated for use in laser mass transfer imaging, but only in the context of ablation transfer. In the field of ablation transfer, it has also long been recognized that spacing apart of donor and receptor is desirable in the interests of improved image quality (see, for example, JP-46-3710 and the 1970 journal article Applied Optics, 9 (No. 10), pp. 2260- 2265). This is confirmed by US-A-5,518,861 and US-A-5,516,622, which disclose, respectively, ablation transfer media having a textured surface (via embossing or similar means) and ablation transfer media comprising spacer beads in the transfer layer. US-A-5,516,622 cautions against placing the beads in the receptor layer.

The need for spacing means in dye sublimation transfer and in ablation mass transfer is largely predictable from first principles. In sublimation transfer, the objective is to transfer dyes in a vaporized state without co-transfer of binder. Preventing the donor layer from actually contacting the receptor layer over most of its area is therefore a logical approach. In the field of ablation transfer, an explosive expansion of gases propels the colorant towards the receptor, and so a gap between the donor and receptor in no way hinders the transfer process. Indeed, by allowing expansion to proceed preferentially in the forward direction, the tendency to expand sideways (causing image spread) is minimized.

Summary of the Invention

Therefore, according to the invention there is provided a method of half tone imaging comprising the steps of:

(a) assembling in mutual contact a receptor sheet and a colorant donor sheet, said colorant donor sheet comprising a support bearing a thermofusible colorant layer comprising a binder, a colorant and an absorber;

(b) exposing the assembly to scanned laser radiation of a wavelength absorbed by said absorber, said laser radiation being focused to a spot of area A μm^2 at the plane of the colorant transfer layer and being modulated in accordance with digital half tone image information, and thereby causing exposed portions of the colorant layer to soften or melt and adhere preferentially to the receptor sheet;

(c) peeling apart said receptor sheet and colorant donor sheet; characterized in that said receptor sheet comprises a support having a textured receptor surface comprising a plurality of protrusions projecting above the plane of the outer surface of said receptor by an average distance of no greater than about 8 μm (preferably, at least 1 μm), there being on average at least 1 of such protrusions per area of A μm^2.

Steps (a) to (c) of the imaging method are preferably repeated one or more times using a different colorant donor sheet comprising a different colorant in each case, but using the same receptor sheet in each case. After steps (a) to (c) have been performed as many times as is necessary, the image-bearing receptor sheet is optionally subjected to a lamination process in which the receptor layer, together with the image residing therein, is transferred to another support.

The outer surface of the receptor refers to the surface of the receptor layer furthest from the support of the receptor, i.e., the surface of the receptor which is presented to the donor. The reference to the plane of the outer surface of the receptor refers to the plane of surface of the layer between the protrusions. The thermofusible colorant layer is one that melts or softens under the action of heat.

It is found that the provision of a surface texture in the receptor, preferably by incorporation of inert particles such as polymer beads, silica, etc., in a receptor layer coated on a support, or alternatively by means of embossing or similar techniques, effectively solves the voiding problems caused by dust particles, and permits channelling and bleeding of air which otherwise might become trapped in pockets between the donor and receptor sheets.

Furthermore, it is surprisingly found that the size and spacing of the protrusions in the receptor surface exerts a profound influence on the quality of the dots transferred thereto, and that by controlling the spacing of the protrusions in accordance with the "footprint" of the exposing laser, high-quality film transfer is enabled, even in the case of large-area images.

Description of Preferred Embodiments

There is very little teaching in the prior art relevant to the use of spacing means in a laser-induced melt transfer system. Indeed, US-A-5,089,372 teaches that conventional melt-transfer to a rough receptor is not possible. US-A-5,501,937 mentions the use of beads, but only as a possibility, without teaching any particular benefit or disclosing any information relating to optimum sizes and spacings. Transfer from a roughened donor to a smooth receptor is stated to be equivalent to transfer from a smooth donor to a roughened receptor. US-A-5,580,693 discloses the incorporation in receptor layers of matting agents in the form of fine particles, but a maximum particle size of 5 µm at a loading of no more than 10 mg/m^2 is taught. This is equivalent to about 200 particles per mm^2. The purpose of the matting agent is to improve the lubricity and handling properties of the sheets, and there is no disclosure of any effect on the image quality.

Consideration of the mechanism of melt transfer, in which the colorant layer must melt or soften and then wet and adhere to the receptor layer, suggests that spacer beads would be detrimental to the process. The melt transfer process necessarily involves intimate contact of donor layer with receptor layer. Spacing beads have a long history of use in the imaging art generally, and the field of laser induced colorant transfer in particular, for the precise purpose of <u>preventing</u> such a contact occurring.

Initial studies lent credence to this pessimistic view. As indicated previously, colorant donor media of the type disclosed in British Patent Application No. 9617414.9 entitled "Crosslinkable Media Imageable by Laser Irradiation," filed August 20, 1996, gave excellent results when imaged to a

smooth receptor, in that the colorant layer was seen to transfer as a coherent film, giving transferred dots with sharp edges. However, the images were unacceptable for commercial purposes owing to the presence of random voids caused by dust particles. When the same donor media were imaged under the same conditions to the beaded receptor used in the Kodak APPROVAL color proofing system, the quality of the transferred image was markedly poorer. Microscopic examination of the image revealed that the colorant layer had fragmented and scattered the pigment particles, giving diffuse dots lacking the sharp edges observed previously. Clearly, the presence of the spacer beads had prevented the colorant layer from transferring as a coherent film. However, it was also observed that voids caused by dust particles were absent.

Subsequent experiments using receptors comprising larger numbers of smaller-sized beads or inorganic particles revealed that as both the diameter of the particles and the average interparticle distance decreased, the degree of non-uniformity in the transferred image also decreased, until a point was reached where the colorant layer once again transferred as a coherent film. Furthermore, this was achieved without the reappearance of voids caused by dust particles, and thus a solution was found to the problem of exploiting the full benefit of LIFT in the context of large-scale images under normal working conditions.

The optimum size and concentration of beads or other particles was found to depend on the dimensions of the footprint of exposing laser, i.e., the diameter of the illuminated spot at the plane of the colorant layer, which determines the minimum size of dot or pixel which can be transferred from donor to receptor. This is typically in the range of about 5 μm to about 50 μm, but may be different for different designs of imaging engine. For example, the Presstek PEARLSETTER imager has a pixel size of about 30 μm diameter, while the Creo TRENDSETTER device has a pixel size of about 8 μm. The concentration of beads or other inert particles in the receptor layer should be sufficient to provide on average at least 1 point of contact per pixel between the donor and receptor layers, preferably at least 2 points of contact. Thus, loadings

of the order of about $5x10^2$ to 10^5 particles per mm^2 are typically found to be useful.

The beads or other particles may be of essentially uniform size (i.e., a monodisperse population), or may vary in size. Dispersions of inorganic particles such as silica generally have a range of particle sizes, whereas monodisperse suspensions of polymer beads are readily available. Whichever type of population is used, the particles should not project above the plane of the surface of the receptor layer by more than about 8 μm on average, but should preferably project above said plane by at least about 1 μm, and more preferably at least about 3 μm. The composition of the polymeric beads is generally chosen such that substantially all of the visible wavelengths (400 nm to 700 nm) are transmitted through the material to provide optical transparency. Non-limiting examples of polymeric beads that have excellent optical transparency include polymethylmethacrylate and polystyrene methacrylate beads, described in US-A-2,701,245; and beads comprising diol dimethacrylate homopolymers or copolymers of these diol dimethacrylates with long chain fatty alcohol esters of methacrylic acid and/or ethylenically unsaturated comonomers, such as stearyl methacrylate/hexanediol diacrylate crosslinked beads, as described in US-A-5,238,736 and US-A-5,310,595.

The shape, surface characteristics, concentration, size, and size distribution of the polymeric beads are selected to optimize performance of the transfer process. The smoothness of the bead surface and shape of the bead may be chosen such that the amount of reflected visible wavelenghts (400 nm to 700 nm) of light is kept to a minimum. This may or may not be an issue depending upon the actual substrate used. For example, if the color proof is formed on a transparent substrate, the haze introduced by the presence of the beads may be effected by the color. The shape of the beads is preferably spherical, oblong, ovoid, or elliptical. In some constructions, it is advantageous to add two distinct sets of beads with different average sizes. This allows the flexibility to balance haze with slip or separation characteristics.

The optimum particle size depends on a number of factors, including the thickness of the receptor layer, the thickness of the colorant layer to be transferred, and the number of colorant layers to be transferred to a given receptor. In the case of transfer of two or more colorant layers to a single receptor, the projections provided by the particles must be great enough not to be obscured by the first layer(s) transferred thereto. If the average projection is significantly greater than about 8 μm, however, transfer of the colorant layer as a coherent film becomes impossible, and the quality of the transferred image deteriorates markedly.

In the case of polydisperse populations of particles, such as silica particles, excellent results have been obtained when the largest of said particles project above the plane of the receptor layer by about 4 μm and provide on average at least 1 point of contact per pixel between the donor and receptor layers, with at least 2 (preferably at least 4) smaller particles also present per pixel. Good results have also been obtained using essentially monodisperse populations of polymer beads projecting about 4 μm above the plane of the receptor layer and providing on average at least 1 point of contact per pixel between the donor and receptor layers.

Surprisingly, incorporation of similar particles at similar loadings in the donor layer, with transfer to a smooth receptor, does not give the same benefits. This is in contrast to what is observed for other modes of laser induced colorant transfer (i.e., ablation and dye sublimation transfer), where the roughened donor/smooth receptor configuration is heavily favoured by the published art.

Receptor elements used in the invention generally comprise a support sheet bearing a receptor layer containing the beads or other inert particles. Preferably, the receptor layer also contains a bleaching agent capable of bleaching the infrared dye which typically co-transfers with the colorant.

The composition of the support sheet is not critical, and essentially any sheet-form material may be used, with flexible materials such as paper or plastic film being preferred. The receptor layer is typically a thermoplastic polymer layer of about 1 μm to about 10 μm, preferably about 1.5 μm to about

5 μm, in thickness. A wide variety of polymers may be employed, provided that a clear, colorless, nontacky film is produced. Within these constraints, selection of polymers for use in the receptor layer is governed largely by compatibility with the colorant intended to be transferred to the receptor, and with the bleaching agent, if used. Vinyl polymers such as polyvinyl butyral (e.g., BUTVAR B-76 supplied by Monsanto), vinyl acetate/vinyl pyrrolidone copolymers (e.g., E735, E535 and E335 supplied by GAF) and styrene butadiene polymers (e.g., PLIOLITE S5A supplied by Goodyear) have been found to be particularly suitable. The receptor layer may be coated directly on the support sheet, or there may be one or more underlayers separating the receptor layer from the support sheet. A particularly advantageous construction is a support sheet coated with a release layer followed by the receptor layer, as this allows the receptor layer (after an image has been transferred thereto) to be transferred to another substrate by a process of lamination followed by peeling of the support sheet. The use of release layers for this purpose is well known in the art, for example, US-A-5,053,381, US-A-5,126,760 and US-A-5,278,576, and suitable materials include fluorinated polymers, silicones, etc.

In preferred embodiments, the receptor layer additionally comprises one or more compounds capable of bleaching the infrared absorber associated with the colorant layer, as disclosed in EP-A-0675003 and British Patent Application No. 9617416 filed Aug. 20, 1996. Preferred bleach agents include amines, such as, diphenylguanidine and salts thereof. The bleach agents are typically used at a loading equivalent to about 5 wt% to about 20 wt% of the receptor layer.

For example, a suitable receptor layer comprises PLIOLITE S5A containing diphenylguanidine as bleach agent (10 wt% of total solids) and beads of poly(stearyl methacrylate) (8 μm diameter) (about 5 wt% of total solids), coated at about 5.9 g/m^2.

A particularly preferred receptor layer is obtained by coating the following formulation from methylethyl ketone (18 wt%) to provide a dry coating weight of 400 mg/ft^2 (4.3 g/m^2):

PLIOLITE S5A	87 wt%
Poly(stearyl methacrylate) beads (8 μm diameter)	1 wt%
Diphenylguanidine	12 wt%

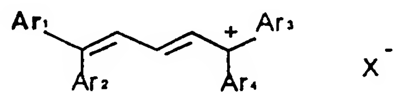
As an alternative to the use of beads or particles the receptor surface may be physically textured to provide the required protrusions. Metal surfaces, such as aluminum, may be textured by graining and anodizing. Other textured surfaces may be obtained by microreplication techniques, such as those disclosed in EP-A-382420.

The extent of the protrusions on the receptor surface, whether formed by bead, particles, or texturing, may be measured, for example, by interferometry or by examination of the surface using an optical or electron microscope.

Colorant donor sheets suitable for use in the invention comprise a support and a thermofusible colorant transfer layer comprising a binder, a colorant and an absorber. The binder is chosen from transparent, film-forming resins, soluble in common organic solvents, which melt or soften at moderately elevated temperatures but do not decompose catastrophically when heated at such temperatures that occur during laser address and film transfer. Most preferably, the binder resin contains functional groups which enable it to participate in curing reactions with other constituents of the colorant layer. A wide variety of commonly-available resins are potentially suitable, and a preferred material is BUTVAR B-76, available from Monsanto.

The absorber used in the invention is a material which will absorb IR or light generating to heat. As absorber (i.e., light-to-heat converter), essentially any dye or pigment may be used, providing it absorbs efficiently at the output wavelength of the intended laser imaging source. Preference is given to infrared-absorbing dyes which are soluble in the binder, and in particular dyes

which are bleachable by reaction with nucleophiles, such as primary or secondary amines, contained in the receptor layer. The preferred class of infrared dyes is that of the tetraarylpolymethine (TAPM) dyes, as disclosed in EP-A-0675003. Such dyes may be represented by the formula:



(1)

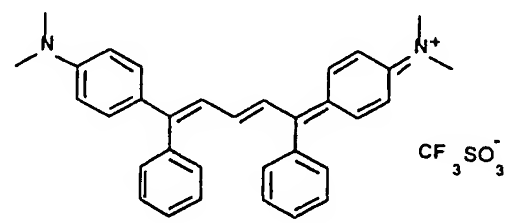
in which Ar^1 to Ar^4 are aryl groups which may be the same or different, and X is an anion.

Preferably, from one to three of the said aryl groups bear a tertiary amino substituent, preferably in the 4-position. Most preferably, at least one but no more than two of said aryl groups bear a tertiary amino substituent. Preferably, Ar^1 or Ar^2 and Ar^3 or Ar^4 bear the tertiary amino substituent. Examples of tertiary amino groups include dialkylamino groups (such as dimethylamino, diethylamino, etc.), diarylamino groups (such as diphenylamino), alkylarylamino groups (such as N-methylanilino), and heterocyclic groups such as pyrrolidino, morpholino or piperidino. The tertiary amino group may form part of a fused ring system, e.g., one or more of Ar^1 to Ar^4 may represent a julolidine group.

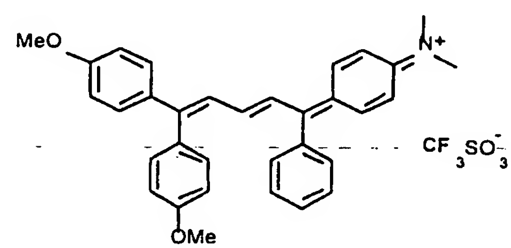
The aryl groups represented by Ar^1 to Ar^4 may comprise phenyl, naphthyl, or other fused ring systems, but phenyl rings are preferred. In addition to the tertiary amino groups discussed previously, substituent which may be present on the rings include alkyl groups (preferably of up to 10 carbon atoms), halogen atoms (such as Cl, Br, etc.), hydroxy groups, thioether groups and alkoxy groups. Substituents which donate electron density to the conjugated system, such as alkoxy groups, are particularly preferred. Substituents, especially alkyl groups of up to 10 carbon atoms or aryl groups of up to 10 ring atoms, may also be present on the polymethine chain. Preferably,

the anion X is derived from a strong acid (e.g., HX should have a pKa of less than 3, preferably less than 1). Suitable identities for X include ClO_4, BF_4, CF_3SO_3, PF_6, AsF_6, SbF_6, and perfluoroethylcyclo-hexylsulphonate.

Preferred dyes of this class include:



D1



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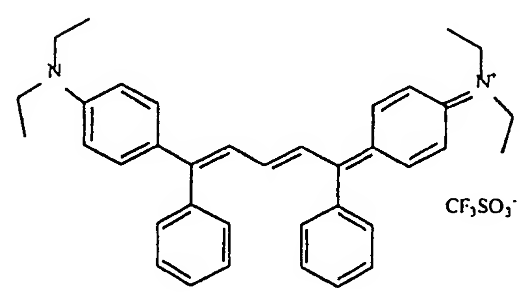


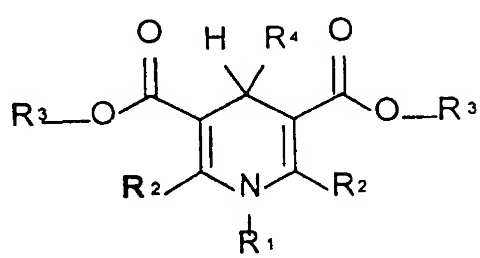
D3

The relevant dyes may be synthesised by known methods, e.g., by conversion of the appropriate benzophenones to the corresponding 1,1-diarylethylenes (by the Wittig reaction, for example), followed by reaction with a trialkyl orthoester in the presence of strong acid HX.

The infrared absorber should be present in sufficient quantity to provide a transmission optical density of at least 0.75, preferably at least 1.0.

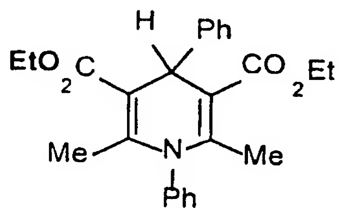
Essentially any colorant may be incorporated in the colorant transfer layer providing the colorant will not sublime under imaging conditions. Suitable colorants include soluble or insolube dyes, dispersions of pigment particles, or mixtures of both dyes and pigments, but pigment dispersions are preferred. Pigments or mixtures of pigments may be employed so as to impart a particular color to the transfer layer, or to confer particular properties thereto such as magnetic properties, pearlescence, opalescence, fluorescence, etc. Blends of pigments as commonly used in the proofing industry and in printing inks are particularly preferred (preferably matching the color references provided by the International Prepress Proofing Association, known as the SWOP color references), and are most preferably used in conjunction with a dispersant, such as DISPERBYK-161, available from BYK-Chemie.

In addition, the colorant transfer layer advantageously may comprise a latent curing agent as disclosed in British Patent Application No. 9617414.9 entitled "Crosslinkable Media Imageable by Laser Irradiation," filed August 20, 1996. Preferred latent curing agents satisfy the formula:

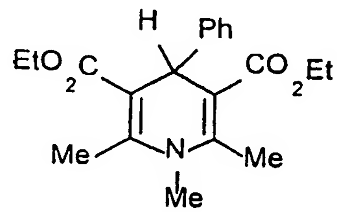


wherein R^1 is H, an alkyl group, a cycloalkyl group, or an aryl group; each R^2 is independently an alkyl group or an aryl group; each R^3 is independently an alkyl group or an aryl group; and R^4 is an aryl group.

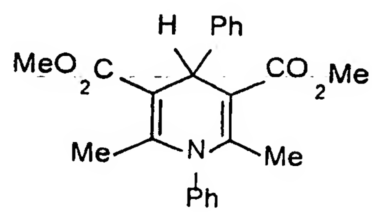
Such compounds are believed to be oxidized during laser exposure to the corresponding pyridinium salts, which can undergo transesterification reactions with hydroxy-functional resins, leading to crosslinking. The process is facilitated by the use, as laser absorber, of cationic dyes such as the above-described TAPM dyes. Preferred latent curing agents include:



C_1



C_2



C_3

In preferred embodiments of the invention, the colorant transfer layer comprises a fluorochemical additive in addition to a dispersion of pigment particles, as disclosed in EP-A-0602893. The use of such an additive in an amount corresponding to at least one part by weight per 20 parts by weight of pigment, preferably at least one part per 10 parts pigment, provides much improved resolution and sensitivity in the laser thermal transfer process. Preferred fluorochemical additives comprise a perfluoroalkyl chain of at least six carbon atoms attached to a polar group such as carboxylic acid, ester, sulphonamide, etc.

Minor amounts of other ingredients may optionally be present in the colorant transfer layer, such as surfactants, coating aids, etc., in accordance with known techniques.

Colorant transfer layers suitable for use in the invention are formed as a coating on a support. The support may be any sheet-form material of suitable thermal and dimensional stability, and for most applications should be transparent to the exposing laser radiation. Polyester film base, of about 20 μm to about 200 μm thickness, is most commonly used, and if necessary may be surface-treated so as to modify its wettability and adhesion to subsequently applied coatings. Such surface treatments include corona discharge treatment, and the application of subbing layers or release layers.

The relative proportions of the components of the colorant transfer layer may vary widely, depending on the particular choice of ingredients and the type of imaging required. Preferred pigmented colorant transfer layers for use in the invention have the following approximate composition (in which all percentages are by weight):

hydroxy-functional film-forming resin (e.g., BUTVAR B76)	35 to 65%
latent curing agent (e.g., C_1, C_2 or C_3)	up to 30%
infrared dye (e.g., D_1 or D_2)	3 to 20%
pigment	10 to 40%
pigment dispersant (e.g., DISPERBYK 161)	1 to 6%
fluorochemical additive (e.g., a perfluoroalkylsulphonamide)	1 to 10%

Thin coatings (e.g., of less than about 3 μm dry thickness) of the above formulation may be transferred to the receptor sheets by laser irradiation in accordance with the invention. Transfer occurs with high sensitivity and resolution, and heating the transferred image for relatively short periods (e.g., one minute or more) at temperatures in excess of about 120°C causes curing and hardening, as well as bleaching of the infrared dye, and hence an image of enhanced durability, uncontaminated by unwanted absorptions is obtained.

Colorant donor elements for use in the invention are readily prepared by dissolving or dispersing the various components in a suitable organic solvent and coating the mixture on a film base. Pigmented transfer media are most conveniently prepared by predispersing the pigment in the binder resin in roughly equal proportions by weight in the presence of a suitable dispersing aid, in accordance with standard procedures used in the color proofing industry, thereby providing pigment "chips." Milling the chips with solvent provides a millbase, to which further resin, solvents, etc., are added as required to give the final coating formulation. Any of the standard coating methods may be employed, such as roller coating, knife coating, gravure coating, bar coating, etc., followed by drying at moderately elevated temperatures.

The procedure for imagewise transfer of colorant from donor to receptor is conventional. The two elements are assembled in intimate face-to-face contact, e.g., by vacuum hold down, and scanned by a suitable laser.

The assembly may be imaged by any of the commonly used lasers, depending on the absorber used, but address by near infrared emitting lasers such as diode lasers and YAG lasers, is preferred. Any of the known scanning devices may be used, e.g., flat-bed scanners, external drum scanners or internal drum scanners. In these devices, the assembly to be imaged is secured to the drum or bed, e.g., by vacuum hold-down, and the laser beam is focused to a spot, e.g., of about 10 μm to about 50 μm diameter, on the IR-absorbing layer of the donor- receptor assembly. This spot is scanned over the entire area to be imaged while the laser output is modulated in accordance with electronically

stored image information. Two or more lasers may scan different areas of the donor receptor assembly simultaneously, and if necessary, the output of two or more lasers may be combined optically into a single spot of higher intensity. Laser address is normally from the donor side, but may be from the receptor side if the receptor is transparent to the laser radiation.

When curing and/or bleaching agents are incorporated in the transfer layer and/or receptor layer, the image residing on the receptor after peeling the donor sheet from the receptor may be further cured and/or bleached by subjecting it to heat treatment, preferably at temperatures in excess of about 120°C. This may be carried out by a variety of means, such as storage in an oven, hot air treatment, contact with a heated platen or passage through a heated roller device. In the case of multicolor imaging, where two or more monochrome images are transferred sequentially to a common receptor, it is more convenient to delay the heating step until all the separate colorant transfer steps have been completed, then provide a single heat treatment for the composite image. However, if the individual transferred images are particularly soft or easily damaged in their uncured state, then it may be necessary to cure and harden each monochrome image prior to transfer of the next, but in preferred embodiments of the invention, this is not necessary.

In some situations, the receptor element of the invention, to which a colorant image is initially transferred, is not the final substrate on which the image is viewed. For example, US-A-5,126,760 discloses thermal transfer of a multicolor image to a first receptor, with subsequent transfer of the composite image to a second receptor for viewing purposes. If this technique is employed in the practice of the present invention, curing and/or bleaching of the image may conveniently be accomplished in the course of the transfer to the second receptor. In this embodiment of the invention, the second receptor may be a flexible sheet-form material such as paper, card, plastic film, etc., and transfer is most readily effected by means of a heated roller laminating device such as a MATCHPRINT laminator. The support sheet of the first receptor element is

then peeled away and discarded, the peeling process being facilitated when a release layer is present between the support sheet and receptor layer.

Advantages of the invention are illustrated by the following examples. However, the particular materials and amounts thereof recited in these examples, as well as other conditions and details, are to be interpreted to apply broadly in the art and should not be construed to unduly limit the invention.

Examples

The invention will now be illustrated by the following Examples in which the following abbreviations, tradenames etc. are used:

BUTVAR B-76	polyvinyl butyral resin supplied by Monsanto, with free hydroxyl content of 7 mole% to 13 mole%
DISPERBYK 161	dispersing agent supplied by BYK-Chemie
MEK	methyl ethyl ketone (butan-2-one)
PET	polyethyleneterephthalate film
SCHOELLER 170M	proofing base supplied by Schoeller comprising silica particles (4 µm to 10 µm diameter) in a resin coating on paper
VIKING base	grained and anodized aluminium printing plate base, obtained by removing the photosensitive coating from VIKING printing plates supplied by Imation
KODAK APPROVAL base	receptor sheet supplied by Kodak as part of the APPROVAL proofing system

Example 1

This Example demonstrates the effect on image quality of varying the surface topography of the receptor layer.

The colorant donor sheet used in this Example comprised the following, as a layer on PET base of approximately 1 μm dry thickness in which all percentages are by weight:

magenta pigment	23.2%
BUTVAR B-76	48.6%
IR Dye D1	9.0%
Curing Agent C1	15.2%
N-ethylperfluorooctylsulfonamide	4.0%

Samples of the donor sheet were mounted face-to-face with samples of various receptor sheets with vacuum hold down on an exposure test bed comprising a fibre-coupled laser diode (500 mW, 870 nm) focused to a 30 μm spot. A half tone dot pattern was imaged on to each receptor under identical conditions of laser power and scan rate, and the quality of each of the transferred images assessed both microscopically (for dot quality) and visually (for overall appearance). The following receptor sheets were tested:

(a) Kodak APPROVAL receptor

(b) an ink jet receptor comprising a coating on paper of starch particles (approximately 500/mm^2, at least 10μm diameter)

(c) Schoeller 170M base

(d) a coating on vesicular polyester of silica particles (4 to 10 μm diameter, approximately 1500/mm^2) in BUTVAR B76 polyvinyl butyral

(e) VIKING printing plate base

(f) a smooth coating on paper of BUTVAR B76 polyvinyl butyral

The results obtained are summarized in the following table:

Receptor	Average Projection (m)	Number per nm^2	Average Number per pixel	Dot Quality	Visual Appearance
(a) comparison	about 20	100	< 1	Very poor (much fragmentation)	Poor color saturation. No dust artefacts
(b) comparison	about 10	500	< 1	Poor (fragmented)	Poor color saturation. No dust artefacts
(c) invention	4 to 6	1500	1 to 2	Good (film transfer)	Bright color. No dust artefacts.
(d) invention	4 to 6	1500	1 to 2	Good (film transfer)	Bright color. No dust artefacts.
(e) invention	< 1	>10000	many	Excellent (film transfer)	Bright color. No dust artefacts.
(f) comparative	-	-	-	Excellent (film transfer)	Bright color. Dust artefacts.

Receptors (a) and (b) gave diffuse images with poor color saturation, whereas receptors (c) to (f) all gave sharp images with bright, saturated color. Microscopic examination revealed that the dots transferred to receptors (a) and (b) had fragmented during the transfer process, with pigment scattered over a wide area, whereas the dots transferred to the other receptors were in the form of coherent films. The dots on receptors (c) and (d) showed some edge distortion, but those on receptors (e) and (f) had sharp edges. However, the image on receptor (f) suffered from "dropouts" caused by dust particles, whereas none of the other images suffered from this defect. Thus, it was concluded that a roughened receptor showing protrusions of on average less than 10 μm, and providing on average at least 1 point of contact per pixel between donor and receptor, is necessary for good quality images, free from dust artefacts. Receptor (e), illustrates the trend for improved image quality as the surface protrusions of the receptor layer become smaller and more numerous.

Example 2

Cyan, magenta, yellow and black (CMYK) donor sheets were prepared as in Example 1 with weight percentages of components listed in the following Table in the thermofusible colorant layer coated at about 1m to SWOP specifications for web off-set printing.

Exposure using Presstek PEARLSETTER 74 running at various scan rates (100 to 500 cm/second) and laser power of 500 mW, 30 micrometer, 870 nm, transfer was effected in the order C, M, Y, K to Schoeller 170M base, the donor-receptor being held in tension together. Blocks of color (10 x 20 mm^2) were imaged over a range of scan speeds (100 to 500 cm/second). A second set from a different color were directly overprinted the first at same scan speed. Successful overprint of C, M, Y, K was achieved with no defects observable over an A2 imaging area, over all scanning speed (100 to 500 cm/second).

Millbases:

Red Shade Cyan Millbase

Red Shade Cyan Pigment	7.77 g
BUTVAR B76	7.77 g
DISPERSBYK 161	0.47 g
MEK	42.0 g
1-methoxy-2-propanol	42.0 g

Phthalo Green Millbase

Phthalo Green Pigment	7.86 g
BUTVAR B76	7.86 g
DISPERSBYK 161	0.47 g
MEK	41.9 g
1-methoxy-2-propanol	41.9 g

Red Shade Magenta Millbase

Red Shade Magenta Pigment	7.78 g
BUTVAR B76	7.78 g
DISPERSBYK 161	0.93 g
MEK	41.8 g
1-methoxy-2-propanol	41.8 g

Blue Shade Magenta Millbase

Blue Shade Magenta Pigment	7.36 g
BUTVAR B76	7.36 g
DISPERSBYK 161	0.88 g
MEK	42.2 g
1-methoxy-2-propanol	42.2 g

Black Millbase

Carbon Black Pigment	9.88 g
BUTVAR B76	9.88 g
DISPERSBYK 161	1.03 g

MEK	39.6 g
1-methoxy-2-propanol	39.6 g

Green Shade Yellow Millbase

Green Shade Yellow Pigment	7.28 g
BUTVAR B76	7.28 g
DISPERSBYK 161	0.44 g
MEK	42.5 g
1-methoxy-2-propanol	42.5 g

Red Shade Yellow Millbase

Red Shade Yellow Pigment	7.28 g
BUTVAR B76	7.28 g
DISPERSBYK 161	0.44 g
MEK	42.5 g
1-methoxy-2-propanol	42.5 g

	Cyan (wgt. in grams)	Magenta (wgt. in grams)	Yellow (wgt. in grams)	Black (wgt. in grams)
Red Shade Cyan Millbase (16% solids in MEK)	12.05			5.16
Phthalo Green Millbase (16.2% solids in MEK)	1.48			
Red Shade Magenta Millbase (16.5% solids in MEK)		20.18		
Blue Shade Magenta Millbase (15.6% solids in MEK)		22.02		1.51
Carbon Black Millbase (20.8% solids in MEK)		0.15		20.09
Green Shade Yellow Millbase (15% solids in MEK)			30.75	
Red Shade Yellow Millbase (15% solids in MEK)			2.69	
BUTVAR B76 (15% solids in MEK; polyvinyl butyral, available form Monsanto)	17.40	0.02	8.91	6.57
IR Dye	1.07	1.23	1.28	0.53
Dihydropyridine	0.39	0.61	0.51	0.45
Fuorocarbon surfactant (7.5% solids in MEK)	0.67	0.67	0.67	0.67
Fluorocarbon polymer (50% solids in MEK)	0.52	0.52	0.73	0.6
Methyl ethyl ketone (MEK)	50.09	44.98	55.14	56.41
Ethanol	9.0	9.0	9.0	9.0
1-methoxy-2- propanol	8.0			

Example 3

A receptor was prepared by coating the following formulation from methylethyl ketone (18 wt%) onto 100 m PET base to provide a dry coating weight of 400 mg/ft^2 (4.3 g/m^2):

PLIOLITE S5A	87 wt%
Poly(stearyl methacrylate) beads (8 diameter)	1 wt%
Diphenylguanidine	12 wt%

The receptor was imaged under the conditions of Example 2 using the cyan, magenta, yellow and black donor sheets. The resulting image was transferred to opaque MATCHPRINT Low Gain base under heat and pressure by passing the receptor and base in contact through a MATCHPRINT laminator. The sheets were peeled apart and the transferred image inspected. The quality of the transferred image was excellent, having good color rendition with no contamination from the IR dye. No dust artefacts were apparent.

The complete disclosure of all patents, patent documents, and publications cited herein are incorporated by reference. The foregoing detailed description and examples have been given for clarity of understanding only. No unnecessary limitations are to be understood therefrom. The invention is not limited to the exact details shown and described, for variations obvious to one skilled in the art will be included within the invention defined by the claims.

What is claimed is:

1. A method of half tone imaging comprising the steps of:

(a) assembling in mutual contact a receptor sheet and a colorant donor sheet, said colorant donor sheet comprising a support bearing a thermofusible colorant layer comprising a binder, a colorant and an absorber;

(b) exposing the assembly to scanned laser radiation of a wavelength absorbed by said absorber, said laser radiation being focused to a spot of area **A** μm^2 at the plane of the colorant transfer layer and being modulated in accordance with digital half tone image information, and thereby causing exposed portions of the colorant layer to soften or melt and adhere preferentially to the receptor sheet;

(c) peeling apart said receptor sheet and colorant donor sheet; characterized in that said receptor sheet comprises a support having a textured receptor layer surface comprising a plurality of protrusions projecting above the plane of the outer surface of said receptor layer by an average distance of no greater than about 8 μm, there being on average at least 1 of such protrusions per area of **A** μm^2.

2. The method of Claim 1 further comprising repeating steps (a) to (c) one or more times using a different colorant but using the same receptor sheet.

3. The method of Claim 1 wherein the resulting image-bearing receptor sheet is subjected to a lamination process wherein the receptor layer together with the image residing therein is transferred to another support.

4. The method of Claim 1 wherein the laser radiation is focused to a spot size of about 5 μm to about 50 μm.

5. The method of Claim 4 wherein the laser radiation is focused to a spot size of about 8 μm to about 30 μm.

6. The method of Claim 1 wherein there is an average of at least two protrusions per area of A μm^2.

7. The method of Claim 6 wherein there is an average of at least four protrusions per area of A μm^2.

8. The method of Claim 1 wherein the protrusions project above the plane of the outer surface of the receptor by about 4 μm.

9. The method of Claim 1 wherein the protrusions are formed by the presence of inert particles or by embossing a receptor layer.

10. The method of Claim 9 wherein the inert particles are selected from polymer beads and silica particles.

11. The method of Claim 1 wherein the receptor layer comprises a thermoplastic polymer in the form of a colorless, non-tacky film.

12. The method of Claim 11 wherein the receptor layer has a thickness of about 1 μm to about 10 μm.

13. The method of Claim 12 wherein the receptor layer has a thickness of about 1.5 μm to about 5 μm.

14. The method of Claim 1 wherein the receptor layer comprises a polyvinyl butyral, a vinyl acetate/vinyl pyrrolidone copolymer, or a styrene butadiene polymer.

15. The method of Claim 1 wherein the receptor comprises a release layer between the support and receptor layer.

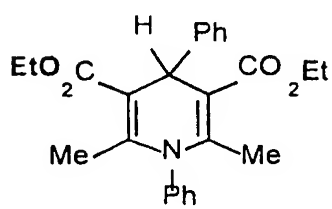
16. The method of Claim 1 wherein the receptor layer further comprises a compound capable of bleaching the absorber of the donor sheet.

17. The method of Claim 16 wherein said compound is diphenylguanidine.

18. The method of Claim 1 wherein the colorant donor sheet comprises a hydroxy-functional film-forming resin.

19. The method of Claim 1 wherein the absorber colorant donor sheet comprises a tetraarylpolymethine dye.

20. The method of Claim 1 wherein the colorant donor sheet further comprises a latent curing agent of the formula:



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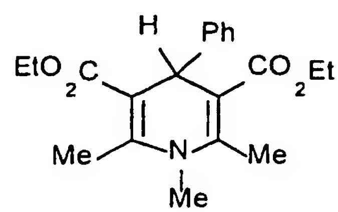
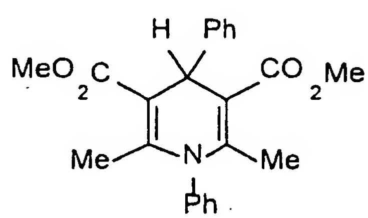


C_2



C_3

21. The method of Claim 1 wherein the colorant donor sheet further comprises a fluorochemical additive comprising a perfluoroalkyl chain of at least six carbon atoms attached to a polar group.

22. The method of Claim 1 wherein the colorant donor sheet comprises a colorant layer comprising:

about 35% to about 65% by weight of a hydroxy-functional film-forming resin;

up to about 30% by weight of a latent curing agent;

about 3% to about 20% by weight of an infrared dye;

about 10% to about 40% by weight of a pigment;

about 1% to about 6% by weight of a pigment dispersant; and

about 1% to about 10% by weight of a fluorochemical additive.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/08095

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B41M5/40 B41M5/38 B41M5/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B41M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 544 283 A (EASTMAN KODAK COMPANY) 2 June 1993 cited in the application see page 2, line 48 - page 3, line 7 see page 5, line 38 - line 47 see claims 1-10; examples 1,2 ---	1-15
A	US 4 876 235 A (C.D.DEBOER) 24 October 1989 cited in the application see column 2, line 7 - line 42 see column 2, line 62 - line 68 see claims 1,4,8,11; examples 1-3 --- -/--	1-22

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
17 July 1998	30/07/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx 31 651 epo nl, Fax: (+31-70) 340-3016	Bacon, A

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Inte onal Application No
PCT/US 98/08095

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
A	US 5 017 547 A (C.D.DEBOER) 21 May 1991 cited in the application see column 2, line 1 - line 20 see column 2, line 53 - line 63 see claims 1-6; examples 1,2 ---	1-22
A	US 5 518 861 A (R.A.COVELESKIE ET AL.) 21 May 1996 cited in the application see column 2, line 6 - line 48 see column 6, line 51 - column 8, line 18 see claims 1,8; examples 1-7 ---	1-22
A	EP 0 675 003 A (MINNESOTA MINING AND MANUFACTURING COMPANY) 4 October 1995 cited in the application see page 2, line 49 - page 3, line 33 see page 3, line 51 - page 4, line 20 see claims 1-19; example 1 -----	1-22

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 98/08095

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